

Intro to Hartree-Fock

- In our discussion of He, H_2^+ , and H_2 , we have used hydrogen-like eigenfunctions as the basis set.
- However, nothing we did relied on using H-atom wavefunctions, per se. The radial wavefunctions in particular can be varied.
- Modifying the basis set to implicitly take into account screening can improve convergence of the results. That is, use basis functions that somehow take into account other electrons, in contrast to H-atom wavefunctions.
- The basic idea of HF is to find an optimal set of radial functions for each electron without solving the full variational problem.

Hartree-Fock and Electron Correlation

- One big challenge in electronic structure calculations is dealing with **electron correlation**: the repulsion between pairs of electrons. If the electrons did not interact with each other, it would be possible to solve the quantum eigenstates exactly.
- Hartree-Fock does NOT treat electron correlation exactly; it only treats it in an average way, iterated to self-consistency.
- Thus, HF does NOT provide exact solutions to the Schrodinger equation, no matter how large a basis set you use!
- Electron correlation can be “added back in” on top of a HF calculation by various methods (essentially by using the variational method, except with basis set defined by HF states). This is referred to as **configuration interaction**.

Self-Consistent Field Method

Basic plan: Pick an initial guess for the wavefunction for some electronic configuration (typically the ground state), which is a product of single-electron wavefunctions:

$$\Psi = \psi_1 \psi_2 \psi_3 \cdots \psi_N$$

[In practice, the total wavefunction is a Slater determinant “spin-orbital”, or a superposition of Slater determinants.]

Now, consider the effects of the other electrons on the wavefunction for, e.g., electron i . We consider each electron other than i to be “smeared out” and “static”, i.e., we represent them as probability distributions that do not depend on the position of electron i :

$$V_i^{eff} = \left(-\frac{Z}{r_i} \right) + \sum_{j \neq i} \int \frac{|\psi_j|^2}{r_{ij}} d\vec{r}_j$$

Charge density for electron j , directly proportional to its probability density.

Coulombic attraction to nucleus; for simplicity we consider an atom, but for a molecule it would just become a sum.

HF-SCF (2)

- Using this “effective potential”, in the field of the other electrons, solve for a new one-electron wavefunction for atom i , ψ_i .
 - Move on to the next electron, and do the same thing.
 - After you’ve gone through all the electrons, go through them all again.
 - Keep doing this until the one-electron wavefunctions stop changing very much (i.e., iterate until you reach “convergence”).
-
- Each step of the SCF procedure is basically a 1D variational problem. So what basis set do we use, and what do we use for the initial guesses?
 - We could use H-atom wavefunctions, but in practice, we use an expansion in terms of some basis set with convenient numerical properties (generally Gaussians) for calculating the many integrals, i.e.,

$$\psi_i = \sum_k c_{ik} \phi_k$$

- This is called the “Hartree-Fock-Roothan” method.

Basis Sets 1: Slater-Type Orbitals (STOs)

These are important primarily for historical reasons, but you still occasionally see them pop up, especially for atomic (i.e., single-atom) HF. But for arbitrary molecules, the integrals are tough to evaluate.

$$\psi(r) = r^{n-1} e^{-kr}$$

Radial form is similar to but simpler than the hydrogen-atom wavefunctions:

$$R_{nl}(r) = -C_{nl} r^l e^{-r/na_0} L_{n+l}^{2l+1} \left(\frac{2r}{na_0} \right)$$

k is the orbital exponent, which can be varied. One choice is

$$k = \frac{Z - \textcircled{s}}{n} \quad \text{“screening parameter”}$$

Basis Sets 2:

Gaussian-Type Orbitals

- These completely dominate modern electronic structure calculations.
- They are actually LESS physically reasonable than the Slater-type orbitals (more later).
- However, they are very convenient for computations. Key property: product of 2 Gaussians centered at different points (nuclei) = 1 Gaussian centered at a third point.
- Basically the HF calculations reduce to calculating integrals that are the product of Gaussians, which can be solved very efficiently.

$$g_{ijk}(x, y, z) = Nx^i y^j z^k e^{-\alpha r^2}$$

These Gaussians are centered on a particular atom.

α = orbital exponent

N = normalization constant

Note that the principal quantum number does not show up!

The same basic functions are used for 1s, 2s, 3s, etc., but with different values of α .

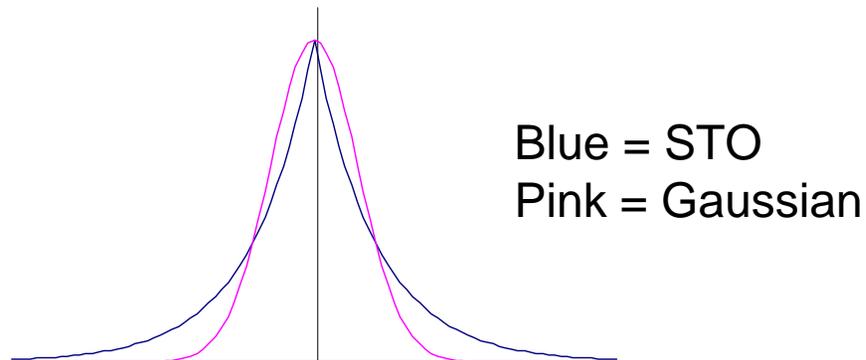
$$g_{ijk}(x, y, z) = Nx^i y^j z^k e^{-\alpha r^2}$$

i	j	k	$i+j+k$	type
0	0	0	0	s
1	0	0	1	p
0	1	0	1	p
0	0	1	1	p
2	0	0	2	d
0	2	0	2	d
0	0	2	2	d
1	1	0	2	d
0	1	1	2	d
1	0	1	2	d

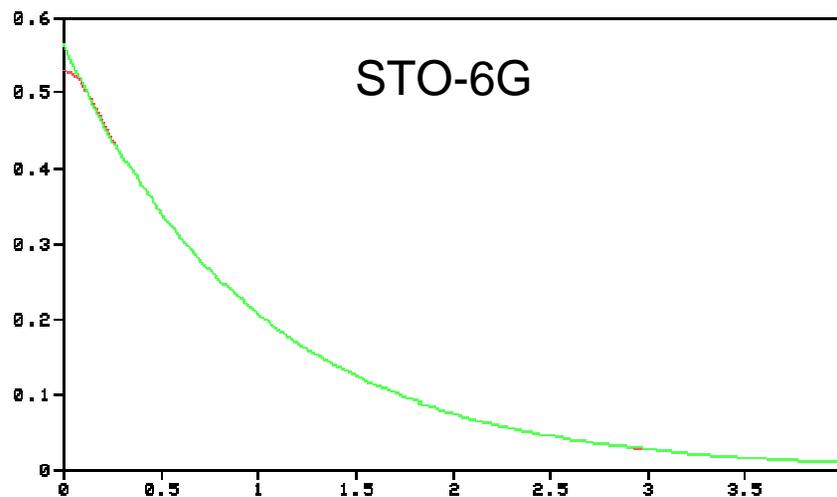
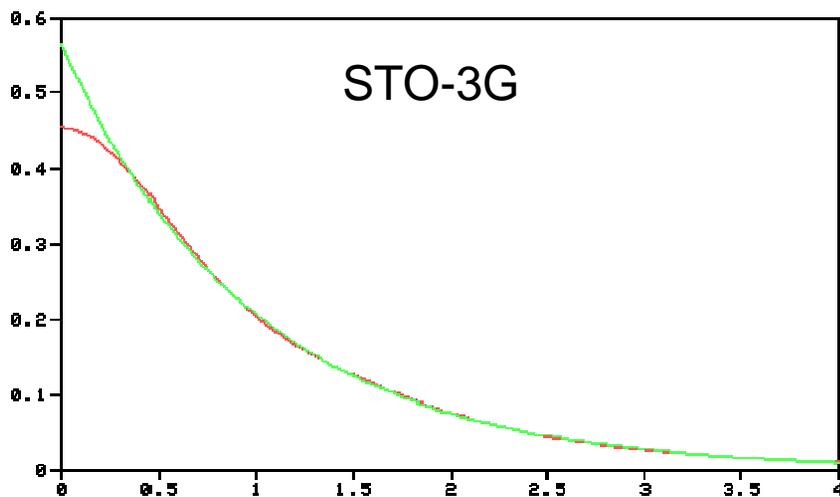
Note that:

- The basis functions have the proper number of nodes
- However, there is one “extra” d-type function (should be 5); can be fixed by taking appropriate linear combinations, x^2-y^2 , $3z^2-r^2$.

Key deficiency of Gaussian orbitals: No cusp at nucleus



Solution: Create “contracted Gaussian functions” expressed in terms of “primitives”. Typically use 3 or 6 Gaussians to approximate STO.



Minimal Basis Sets and Beyond

Minimal Basis

1 basis function for each atomic orbital

H: 1 (1s)

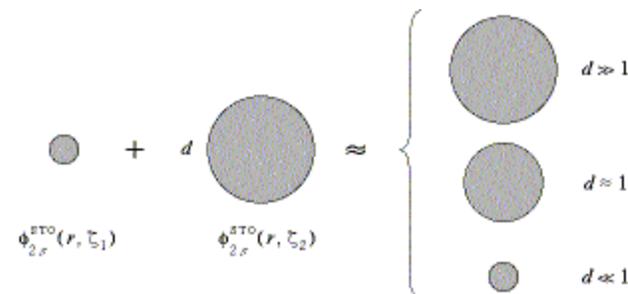
C: 5 (1s, 2s, 2p_x, 2p_y, 2p_z)

**Example:
STO-3G**

Split Valence

Problem: Size of orbitals held fixed for all systems.

Solution: Double (or even triple) the number of basis functions for each orbital, with different orbital exponents (widths, sometimes called “zeta”).



Double Zeta: 2 basis functions for each orbital

**H: 2
C: 10**

Triple Zeta: 3 basis functions for each orbital

**H: 3
C: 15**

**Example:
6-311G**

Split Valence: 1 basis function for each core orbital, but 2 for valence.

**H: 2
C: 9** **Example:
3-21G**

Diffuse Functions

Problem: When dealing with systems with lone pairs, anions, and excited states, electrons can move far from the nucleus.

Example:
6-31G+

Solution: Introduce “diffuse functions”, really large basis functions.

Polarization Functions

Problem: Basis functions are isotropic around the nucleus, but bonding (or hydrogen bonding) introduces anisotropy.

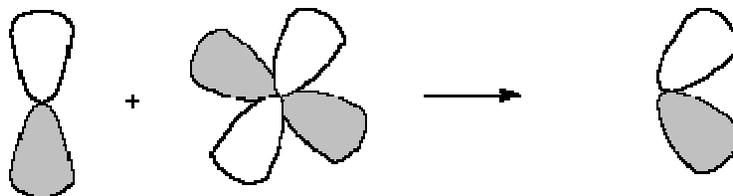
Solution: Introduce “polarization functions” to permit anisotropy.

For p orbitals, add in d functions (6 of them)

Example:
6-31G* = 6-31G(d)

For s orbitals, add in p functions (3 of them)

Example:
6-31G** = 6-31G(d,p)



Polarization of a p orbital by mixing with a d function

What the basis set names mean

6-311+G**

**Each inner shell
(core) basis
function composed
of 6 primitives**

**Triple-zeta split
valence basis: One
is contracted
function of 3
primitives, and the
other two are single
Gaussians**

**Add diffuse
functions**

**Polarization of
p-orbitals with
d functions**

**Polarization of
s-orbitals with
p functions**

Alphabet Soup: A Sampling of Basis Sets

Basis Set	Orbitals for H atoms	Orbitals for 1st row atoms	Comment
STO-3G	1	5	Minimal
3-21G	2	9	Split Valence
6-31G*	2	15	Add polarization for heavy atoms
6-31G**	5	15	Add polarization for H atoms
6-31+G**	5	19	Add diffuse functions
6-311+G**	6	22	Triple zeta valence

Tricks of the Trade

- Computational expense is N^4 , where N is the number of basis functions.
- For example, 400 basis functions (medium size molecule) gives $\sim 10^9$ integrals to evaluate.
- Can reduce this to some extent by exploiting the fact that some matrix elements are equal to each other (factor of 8), or if the molecule has symmetry, e.g., water (C_{2v}).
- For large molecules, can skip integrals that are likely to be very small, because they involve basis functions on atoms that are quite far from each other (can approach N^2 scaling).
- In the end, you still probably have to use the hard disk to store all the integrals you need, or recalculate them on the fly.
- One other extremely useful method is the use of pseudospectral basis sets. This is a little beyond the scope of this course, but it essentially makes the integrals much easier to calculate, and reduces the overall scaling to N^3 . This is what is used in Jaguar, and makes it much faster than Gaussian for large systems.

Back to configuration interaction

Hartree-Fock, at least with a sufficiently large basis set, can predict lots of properties with reasonable accuracy, e.g., equilibrium structures and relative energies. But there are some notable failures ...

Example: CO dipole moment

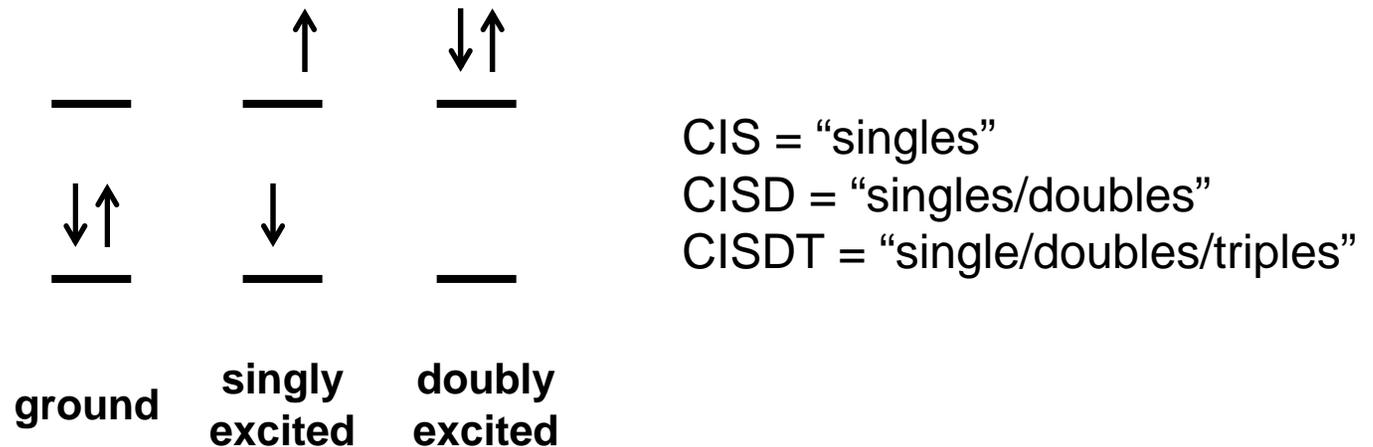
Experiment	-0.11 D	C-O+
HF (large basis)	+0.27 D	C+O-
HF + CI	-0.12 D	

Example: Dissociation energies

Molecule	Experiment	HF
N ₂	9.9 eV	5.3 eV
F ₂	1.6 eV	-1.4 eV

HF + CI

- Remember, HF only treats electron correlation in an average, not instantaneous sense.
- Put a different way, HF provides optimal molecular orbitals (at least with a large basis), but the configurations built from the MOs are themselves coupled due to instantaneous electron correlation.



Now do variational calculation using configurations with the same symmetry.

Full CI

of MOs = # of basis functions

of configurations increases roughly as b^n
where b = # of basis functions
and n = # of electrons

Note that doing full CI with a small basis is a waste of time.

OUCH

But some configurations will be much more important than others.
Common strategy: focus only on excitations of valence electrons
("frozen core").

Multiconfiguration CI

MCSCF (multiconfiguration SCF)

Basic idea: Instead of holding the HF-SCF MOs fixed for the CI calculation, allow them to variationally optimize during the CI phase as well as the CI coefficients. It's like you're doing HF except with multiple configurations explicitly included.

CASSCF (complete active space SCF)

Basic idea: Just like MCSCF, except with only certain excitations included. Divide the orbitals into active (typically valence) and inactive (typically core) sets. All excited configurations involving active orbitals are used.

Scaling: Formally, about b^8 , where b is the number of basis functions, although it can be reduced to about b^5 by pre-computing many terms.

Moller-Plesset Perturbation Theory

- Basic idea: Treat instantaneous electron correlation as a perturbation to the HF-SCF solutions. In other words, the perturbation is the difference between the exact $1/r_{12}$ coupling and the SCF solution. Much more efficient than full CI!
- The HF-SCF, with a large basis set, is in fact the correct 1st-order perturbation theory result for electron correlation. So the first new term is the 2nd order perturbation theory result. This is “MP2”.
- There are also higher order theories, i.e., MP3, MP4. As with all perturbation theory, higher order does not guarantee higher accuracy. [And in fact, going to higher and higher order is not at all guaranteed to converge on the right answer.]
- Need a good basis set! Frequently used basis sets include the Dunning sets:

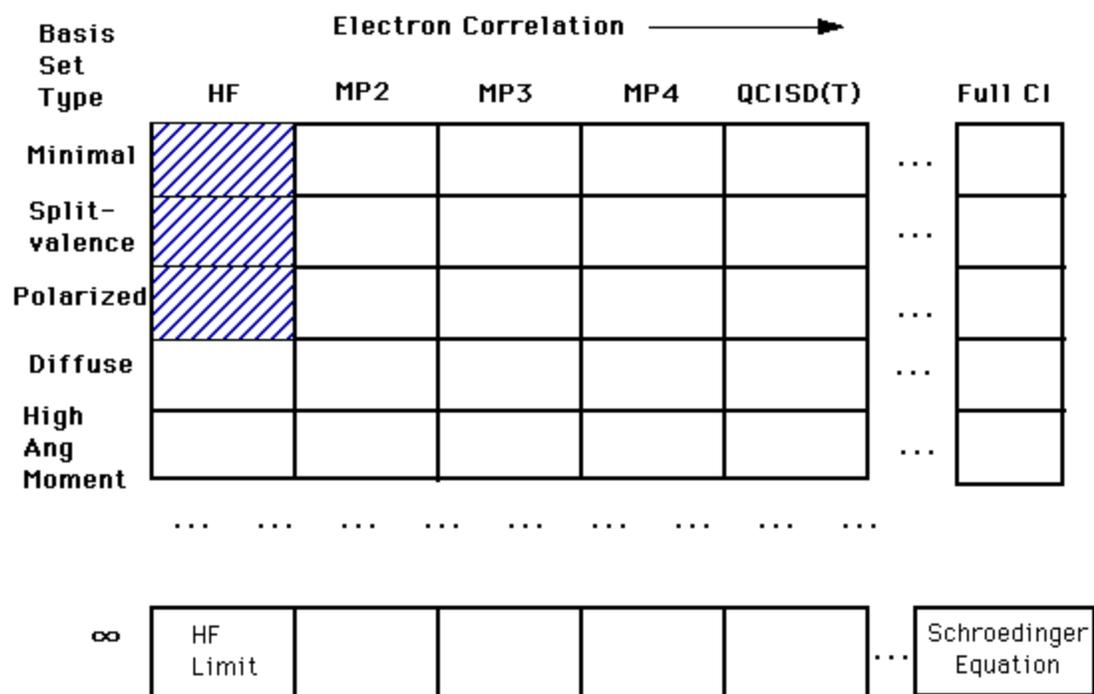
cc-pVDZ
diffuse (aug)-cc-pVTZ “polarization
functions “correlation Valence Triple Zeta”
consistent”

- These have a little different philosophy: develop contractions by SCF calculations on atoms, thus building some electron correlation into basis set.
- Frozen core approximation often invoked for MP calculations as well.

LMP2

- “Local” MP2
- Basic idea: Try to reduce the effort by recognizing that, in large systems, electrons really do tend to be localized. [One of many attempts to reduce horrible scaling of QM by exploiting locality.]
- Transform from original set of MOs to new localized MOs.
- Only consider excitations that remain localized near atoms involved in the localized ground state MO.

High Accuracy Requires Large Basis Set and Some CI



Density Functional Theory

- The fundamental idea: The ground state energy, wavefunction, and all other observables are uniquely determined by the total electron probability density: $\rho(x,y,z)$.
- This density is a function of only 3 variables, not $3N!$
- More precisely, energy and other observables are “functionals” of ρ
 - function: associate a number with variables
 - functional: associate a number with a function
- Moreover, a variational principle applies such that the true ground state ρ is the density that minimizes $E[\rho]$. This is the Hohenberg-Kohn variational theorem.
- As before, we divide the Hamiltonian into 3 parts (kinetic, electron-nuclear attraction, and electron-electron repulsion):

$$\hat{H} = \hat{T} + V_{Ne} + V_{ee}$$

- Each of these components is individually a functional of ρ .

DFT: The External Potential

In DFT language, the attractive potential between the electrons and nuclei is referred to as the “external potential”.

$$V_{Ne} = \sum_i V_N(\vec{r}_i)$$

$$V_N(\vec{r}_i) = -\sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}}$$

$$\overline{V_{Ne}} = \int |\psi_0|^2 V_{Ne} = \int |\psi_0|^2 \sum_i V_N(\vec{r}_i) = \int \rho(\vec{r}) V_N(\vec{r}) d\vec{r}$$

In the last step, we collapse the sum to indicate the overall nuclear potential at any point.

This indicates that we know the functional for this part of the Hamiltonian!

The Kohn-Sham Method

- The functionals for the kinetic energy and electron-electron repulsion part of the Hamiltonian remain unknown. So we haven't gotten very far yet ...
- This is where the Kohn-Sham method comes in.
- The logic is a bit convoluted, but what it buys us is the ability to shove all of the parts of $T[\rho]$ and $V_{ee}[\rho]$ that are hard to calculate into a single term, $E_{xc}[\rho]$, which is generally small and can be approximated in various ways.
- “XC” stands for “exchange and correlation”, the key effects that need to be accounted for in the made-up functional.
- Note that in HF, the exchange term is treated correctly, but, as we know, correlation effects are only approximate (without using CI methods).
- If DFT, exchange is dealt with approximately, but some effects of correlation are dealt with at the same time.
- In my opinion, DFT can be considered a semi-empirical method, because in the end, the XC functional is given a functional form, and you fit parameters to get good answers. In contrast to other semi-empirical methods (next lecture), it is founded on a much more solid theoretical basis.

XC Functionals

1. LDA: Local density approximation. Basic idea is to approximate $E_{xc}[\rho]$ using the exchange and correlation energy of “jellium”: a homogeneous electron gas with density ρ (but electrically neutral). Valid if electron density changes slowly with position. Not sufficiently accurate for most purposes.
2. $X\alpha$: Correlation entirely omitted. Originally developed by Slater as an approximation to HF. Similar to LDA approximation.
3. Gradient-corrected functionals: Most modern functionals fall into this category. Basic idea: make the functional depend not only on ρ but also

$$\nabla\rho$$

The gradient part accounts for rate of change in density, which is ignored in LDA. Also called a “nonlocal” functional.

- Most important gradient-corrected *exchange* functional due to Becke (1988): B88. Uses LDA but adds in new complicated term involving gradient and an empirical parameter, fit to HF exchange energies.
 - Most important gradient-corrected *correlation* functional due to Lee-Yang-Parr: LYP.
 - Put them together and you get “BLYP”.
4. Hybrid functionals. Calculate exchange integrals explicitly as in HF, and then combine this term with functionals, e.g., “B3LYP” (“3”=3 parameters).